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Remarkable Polymorphism in Gels of New Azobenzene Bis-urea Gelators†

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Azobenzenes substituted with two urea groups, and especially the 2,2′-disubstituted azobenzenes, form thermoreversible gels with a wide range of organic solvents at concentrations which are in some cases even as low as 0.2 mM. Most remarkably, the 2,2′-disubstituted azobenzene gelator can form two different morphs, which is governed by the properties of the solvent and kinetic factors.

Introduction

The self-assembly of small functional molecules into supramolecular structures comprises a powerful approach toward the development of new materials and devices of nanoscale dimensions,[1,2] and the control of these organizational processes by chemical or physical elements is a major challenge. A promising approach toward such responsive or smart materials is the integration of an addressable function, e.g., photochromic moieties, into the supramolecular building blocks, which would offer the possibility to alter the self-assembly process of the individual molecules or change the properties of the supramolecular arrays by means of light.[3] A number of photoresponsive host−guest systems and receptors[4] have been reported, but studies of self-assembling photoswitchable systems, in which the macroscopic properties are affected by light, are limited to a few examples. Switchable organogels have been reported by Shinkai et al. almost a decade ago,[5] and more recently by Pozzo et al.,[6] whereas the photoreversible self-assembly of peptide tubes has been reported by Ghadiri et al.[7] Recently our group showed that the extension of dithienylcyclopentene photochromic switches with strongly interacting groups such as amides gave highly viscous solutions with apolar solvents due to extensive aggregation of the compounds. Most remarkably, the degree of aggregation and hence the viscosity can reversibly be changed by light.[8]

In recent years there has been significant progress in the rational design of new gelling agents, and from successful designs it has emerged that the presence of strong self-complementarity and unidirectional interactions are essential features for a good gelling agent.[9,10] Urea moieties fulfill these requirements, and especially compounds that contain two urea groups have been reported to be very potent and versatile gelling agents for a wide range of organic solvents.[11,12] Previously it has been shown that the conformational properties of the linking group between the urea moieties strongly influence the gelation ability and properties. The replacement of a static linking group by a functional molecule whose properties respond to some external stimulus might thus well lead to the formation of responsive gels. Here we report on new azobenzene bis-urea gelling agents, in which the azobenzene group has been used to link the two urea groups, and a first study of their gelation behavior by microscopic and spectroscopic techniques.

Results and Discussion

The 4,4′-disubstituted azobenzene **1** and 2,2′-disubstituted azobenzene **2** represent two structurally relatively simple bis-urea azobenzenes (Chart 1). These compounds have, however, all the primary prerequisites for a gelling agent, i.e., two strongly interacting self-complementary groups in combination with a linker that directs these groups along a common axis, thus favoring the formation

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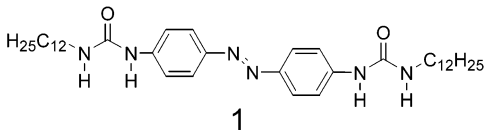
Chart 1



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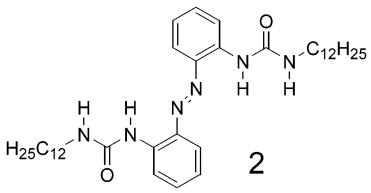

2

Table 1. Gelation of Organic Solvents by Azobenzene Bis-ureas[a]

solvent	1	2	solvent	1	2
ethanol	p	8	cyclohexanon	p	p
DMSO	p	p	cyclohexane	i	1.5
dichloromethane	p	1.5	*p*-xylene	8	1.5
2-propanol	p	3	1,2-dichloroethane	p	3
toluene	8	0.8	*n*-butyl acetate	p	8
hexane	i	0.2	tetralin	8	1.5

[a] Minimum gelation concentrations in mM: p = precipitation; i = insoluble; s = soluble.

of infinite quasi-1D aggregates. Compounds **1** and **2** are easily synthesized by an addition reaction of the corresponding bis-aminoazobenzenes with an isocyanate. Usually this reaction proceeds rapidly at room temperature, but in this case the reaction proceeded relatively slowly due to the decreased nucleophilicity of the aniline-type amine groups, and reflux in toluene was found to be necessary to obtain **1** and **2** in a reasonable yield of 83% and 40%, respectively. The relatively low yield of **2** is most likely caused by its efficient gelation of the reaction mixture which begins even at low conversions, thereby preventing stirring and slowing down mass transport.

Bis-urea azobenzenes **1** and **2** are almost insoluble in most organic solvents at room temperature, but upon heating they gradually dissolve. In apolar solvents such as hexane or cyclohexane compound **1** did not dissolve at all, even after prolonged heating at temperatures above the boiling point of the solvent. Upon cooling to room temperature, **1** precipitates from most solvents. Only with aromatic solvents gels were formed (Table 1). These gels had a turbid appearance and were easily and irreversibly disrupted by mechanical agitation like shaking or vortexing, indicating that aggregates of macoscopic dimensions have been formed. Light microscopy revealed that toluene gels of **1** consist of thin elongated fibers of macroscopic dimensions, with diameters up to 5 μm (Figure 1a). The fibers are strongly birefringent, indicating a well-defined molecular arrangement within the fibers. The formation of similar fibers has been commonly observed for other bis-urea compounds in which the two urea groups are connected by a linear linker.[11a]

Azobenzene bis-urea **2** behaves much differently. It dissolves at considerably lower temperatures and to higher maximum concentrations than **1** in all solvents investigated including hexane and cyclohexane. Moreover, upon cooling of hot solutions gels are formed with all solvents investigated, except for cyclohexanone and polar solvents such as DMSO and water (not shown) (Table 1). In all cases the minimum gelation concentrations are less than 8 mM, and in toluene and *n*-hexane very fragile gels are even formed at concentrations as low as 0.2 mM, which is comparable to those of the recently reported "super-

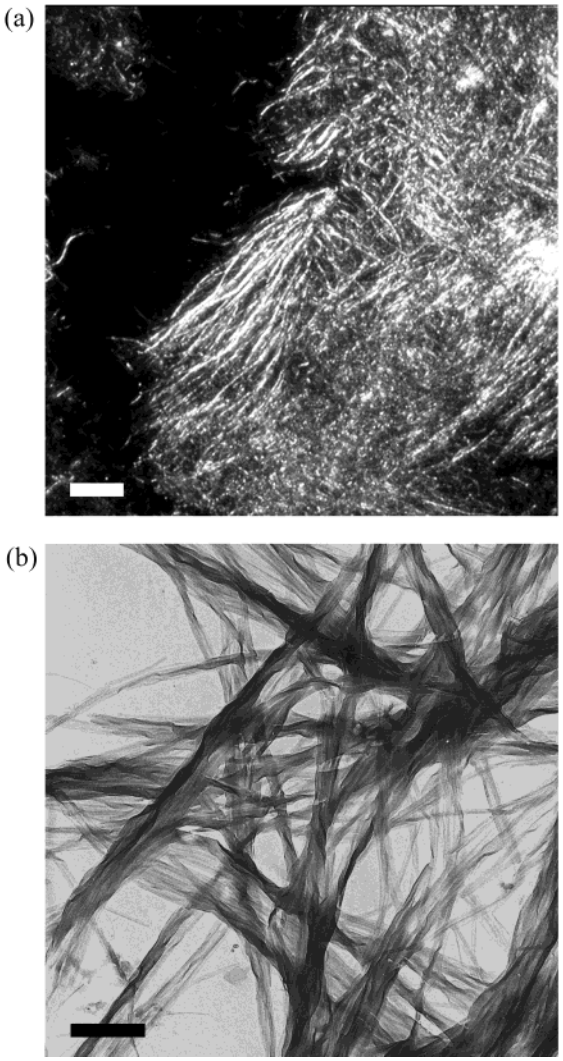

Figure 1. (a) Optical microscopy of a toluene gel of **1** (7.9 mM) between crossed polarizers (bar = 50 μm) and (b) cryo electron microscopy of a toluene gel of **2** (1.6 mM, bar = 400 nm).

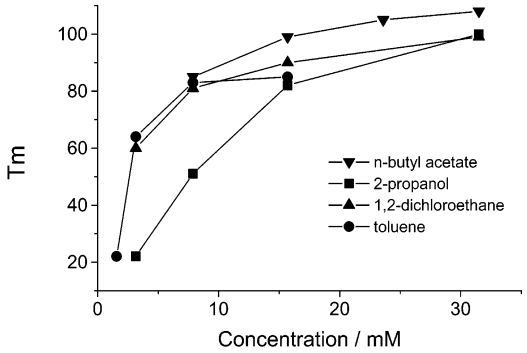

Figure 2. Gel-to-sol phase transition temperatures of gels of **2** in various solvents as determined by the dropping ball method.

gelators".[13] Gels can be formed up to concentrations of at least 30 mM, and these exhibit excellent thermal stability with melting temperatures exceeding 100 °C at higher concentrations for the *n*-butyl acetate gels (Figure 2).

Furthermore, gels of **2** are optically transparent and optical microscopy did not reveal any structural features. The morphology of a toluene gel of **2** was further studied by cryo electron microscopy. Because the melting point of

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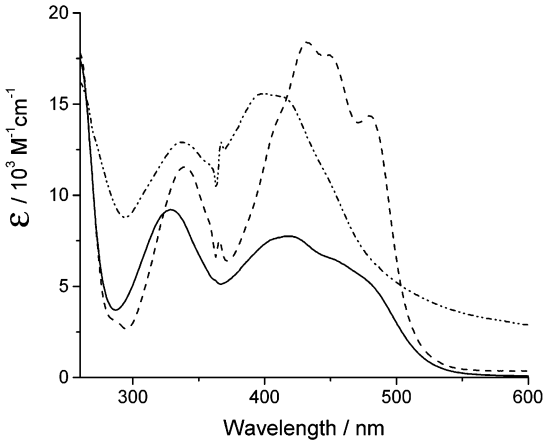

Figure 3. Absorption spectra of a solution of **2** in 1,2-dichloroethane (0.1 mM, —) and of a gel in 1,2-dichloroethane (1.85 mM, — - -) and in cyclohexane (2.37 mM, — —) at 25 °C.

toluene (−95 °C) is rather high compared to liquid nitrogen, thin samples could be rapidly frozen in a nitrogen slush to give a matrix of amorphous solid toluene without any crystallites. Within this frozen toluene matrix, the fibrous network formed by **2** is clearly visible (Figure 1b). Compound **2** forms thin, flat fibers, which are occasionally twisted and which form junction zones through fusion and splitting. The fibers formed by **2** are polydisperse and can be as thick as 200 nm, but from the micrographs it can be seen that these thicker fibers consist of bundles of thinner fibers. Furthermore these thinner fibers are not monodisperse and are between 10 and 20 nm thick. The high aspect ratio of the fibers indicates that they are formed through a highly anisotropic growth process. In many regards, the properties of gels of **2** are reminiscent of gels formed by cyclic bis-urea compounds previously reported by our group.[11b]

Chromophores such as azobenzenes often show a pronounced effect of aggregation on their electronic absorption spectra, due to exciton coupling between the chromophores in the aggregated state.[14] In the case of **2**, it is readily observed that gelation is accompanied by a color change from orange/red in solution to bright yellow in the gel state. However, in apolar solvents such as toluene and cyclohexane the color change is less pronounced and the gels have an orange color. The electronic absorption spectrum of a 1,2-dichloroethane solution of **2** well below the minimum gelation concentration is shown in Figure 3. This spectrum is characteristic of an azobenzene with two electron-donating substituents such as urea moieties,[15] and the band at 419 nm and shoulder at 470 nm are interpreted as the $\pi\pi^*$ and $n\pi^*$ transitions of the azobenzene, respectively.[16] The absorptions obey Beers law, which indicates that under these conditions azobenzene **2** is not aggregated. The electronic absorption spectra of gels of **2** look completely different. In gels of more polar solvents, like ethanol, ethyl acetate, and 1,2-dichloroethane, the absorption at 419 nm has shifted to 400 nm (Figure 3). This blue shift can be attributed to exciton coupling between neigboring azobenzene moieties in aggregates of **2,** which are present in the gel phase, and shows that there is a direct electronic interaction between the azobenzene chromophores within the aggregates. According to Kasha's exciton coupling theory the blue shift points to the formation of face-to-face type of aggregates.[17] On the other hand, in apolar solvent like cyclohexane gelation causes a shift of the $\pi\pi^*$ transition to longer wavelengths together with the appearance of a vibronic structure with maximum intensity at 433 nm. The appearance of this vibronic structure, however, complicates the interpretation of spectral changes in relation to the supramolecular structure of the aggregates by a simple model as Kasha's exciton coupling theory. Nevertheless, from the distinct changes in the absorption spectra going from solution to the gel phase, it is evident that different types of aggregates are formed in more polar and in apolar solvents, from hereon referred to as type I and type II aggregates, respectively.

The structure of the gels was further investigated by infrared spectroscopy and small-angle X-ray scattering (SAXS). Type I gels of **2** in $CHCl_3$ show two almost overlapping NH vibrations at 3335 and 3310 cm^{-1}, and two sharp bands at 1640 and 1554 cm^{-1}, which can be assigned to the amide I and amide II band, respectively.[18] The positions of these bands are only slightly different from the positions in the solid state at 3324, 1634, and 1557 cm^{-1} for the NH, amide I and II bands, respectively, and clearly show that the urea groups participate in a hydrogen-bonded network.[19] Type II gels of **2** in cyclohexane show a different pattern. The NH vibrations are slightly broadened and shifted to 3344 and 3320 cm^{-1}, and the amide I band is shifted to 1646 cm^{-1}. Most remarkably, the amide II band is split into two broad bands with maxima at 1563 and 1524 cm^{-1}. Although the position of the amide I vibration clearly indicates that both the urea groups of **2** are still involved in hydrogen bonding, the splitting of the amide II bands reveals that they are no longer equivalent. Apparently, the hydrogen bonding network of type I and type II gels of **2** formed in chloroform and cyclohexane, respectively, is different. To further support the formation of different morphs by bisurea azobenzene **2,** SAXS experiments have been carried out. For type I gels of **2** in ethanol a clear Bragg peak was observed at a Q value of 0.26 $Å^{-1}$, corresponding to a spacing of 24 Å, but for type II gels of azobenzene **2** in cyclohexane, no Bragg reflections were observed at all. These results indicate that azobenzene **2** adopt a different molecular arrangement in type I and type II gels, but the actual arrangements within the gels remain unclear because of the absence of higher order reflections.

The distinct spectroscopic changes accompanying gel formation offer an excellent tool to investigate the mechanism of gelation by spectroscopic methods. A surprising result has been found for the gelation of toluene by **2**. Cooling of a toluene solution of **2** from above the gel-to-sol phase transition temperature to room temperature causes in the first few minutes a red shift and increase of the intensity of the $\pi\pi^*$ transition together with the appearance of a vibronic structure (Figure 4). As shown above, this spectral change is typical for the formation of type II aggregates such as is observed in gels of **2** cyclohexane. Most likely, the initially formed aggregate in toluene has a similar structure. Within 10−60 min, depending on the concentration, the intensity of this band at 433 nm decreases and transforms slowly to a spectrum with a maximum at 391 nm which is typical for type I aggregates such as the gels of **2** in more polar solvents. Apparently,

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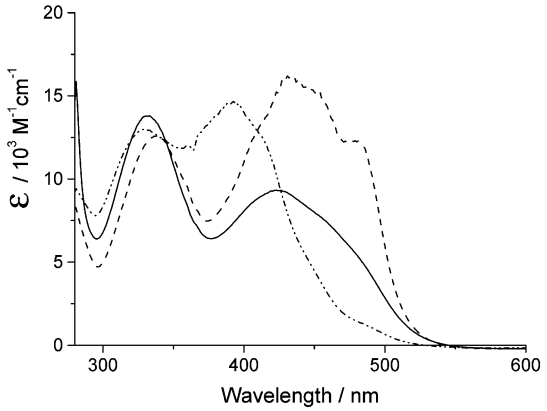

Figure 4. Absorption spectra of a solution of **2** in toluene (1.26 mM) at 70 °C (—) and of a gel obtained directly after cooling to 25 °C (– –) and after 30 min (– - -).

in toluene compound **2** first assembles into the kinetically favored type II aggregates, which over time slowly transform into the thermodynamically favored type I aggregates. The time traces and concentration dependencies showed that the kinetics of these processes are very complex. Preliminary experiments revealed that the rate of transformation of type II into type I aggregates is slowed at lower temperatures and at 0 °C the type II aggregates are stable for several hours. Most remarkably, the rate of transformation of type II into type I aggregates is also slowed with increasing concentration of **2**, a result which is contrary to that expected for classical first- or second-order processes and which can only be explained by including the state of aggregation into the kinetic model.

In conclusion, whereas the 4,4′-disubstituted azobenzene bis-urea **1** is a rather poor gelator and resembles in this regard other "linear" types of bis-urea gelling agents, the 2,2′-disubstitued derivative **2** is an excellent gelator for a wide range of solvents, even at very low concentrations. Most remarkably, the electronic and infrared spectroscopic investigations of the gels clearly indicate that **2** can form two types of supramolecular aggregates depending on the polarity of the solvent, which differ in the stacking of the chromophore moiety as well as the hydrogen bonding pattern. Although polymorphism is well-known phenomena in molecular crystallography,[20] this is probably one of the first examples in the field of organogels. The preliminary results of gelation of toluene indicate that two morphs have different thermodynamic stabilities, but their formation is determined by kinetics. Although the supramolecular arrangement within the different morphs is not yet clear, the azobenzene bis-urea gelling agent forms in this regard an ideal model system for mechanistic investigations of polymorph formation because of the distinct spectroscopic changes which accompany formation of the two morphs. Another intriguing aspect, especially in relation to the polymorphism, is the photochromism of the bis-urea azobenzenes which is currently under investigation.

Experimental Section

Materials and Methods. 4,4′-Diaminoazobenzene[21] and 2,2′-diaminoazobenzene[22] were prepared according to literature procedures. All other compounds are commercially available (Aldrich, ACROS) and were used without further purification. Toluene was distilled from sodium prior to use. Solvents for gelation experiments were of analytical grade and used as received. FTIR spectra were recorded on a Matthson Instruments 4020 Galaxy series FT-IR apparatus, and UV−vis spectra were recorded on HP8453 photodiode array spectrometers.

4,4′-Bis(3-dodecyl-ureido)-azobenzene (1). Dodecylisocyanate (0.242 g, 1.15 mmol) was added to a suspension of 4,4′-diaminoazobenzene (0.107 g, 0.505 mmol) in dry toluene (10 mL) and heated to reflux. After being stirred for 20 h at reflux temperature, the reaction mixture was allowed to cool to room temperature. The product separated as a light brown precipitate, which was isolated by filtration, and purified by repeated precipitation from ethanol. After drying at 40 °C under reduced pressure, the product was obtained as a yellow-brown solid. Yield 0.178 g (0.421 mmol, 83%). ^{1}H NMR (DMSO, 100 °C.): δ = 0.84-(t, 6H); 1.24 (m, 36H); 1.45 (t, 4H); 3.10 (t, 4H); 6.08 (s, 2H); 7.36 (d, 4H); 7.71 (d, 4H); 8.54 (s, 2H). IR (Nujol, cm^{-1}): 723 (m), 849(m), 1103(w), 1165(w), 1238(m), 1310(w), 1377(s), 1410(w), 1562(s), 1601(m), 1630(s), 1713(w), 2855(s), 2926(s), 2955(s), 3302-(m), 3325(m). MS (CI+) *m/z*: 635 (M^+ + 1); Anal. Calcd for $C_{38}H_{62}N_6O_2$: C, 71.88; H, 9.84; N, 13.24. Found: C, 70.8; H, 9.5; N, 13.1. The very poor solubility of the product prohibited further purification to obtain an analytically pure sample.

2,2′-Bis(3-dodecyl-ureido)-azobenzene (2). Dodecylisocyanate (0.5 g, 2.37 mmol) was added to a suspension of 2,2′-diaminoazobenzene (0.215 g, 1.0 mmol) in dry toluene (10 mL) and heated to reflux. After being stirred for 48 h at reflux temperature, the reaction mixture was allowed to cool to room temperature. The resulting red-brown jelly-like reaction mixture was filtered under suction, and the waxy residue rinsed with toluene and acetone and dried in an oven at 80 °C and 1 mbar. The crude material is purified by dissolving it in hot ethanol, filtration of the hot solution to remove traces of insoluble material, cooling to room temperature, and isolation of the product by filtration. This procedure was repeated by using toluene/butanol (4/1 v/v) as the solvent. After drying at 40 °C under reduced pressure, the product was obtained as an orange solid. Yield = 0.53 g (0.84 mmol, 83%). ^{1}H NMR ($CDCl_3$) δ = 0.84(t, 6H); 1.24 (m, 36H); 1.52 (t, 4H); 3.22 (t, 4H); 5.34 (s, 2H); 7.06 (t, 2H); 7.36 (t, 2H); 7.69 (d, 2H); 8.15 (d, 2H); 8,42 (s, 2H). ^{13}C NMR (500 MHz, DMSO/toluene 3:1, 100 °C): δ = 14.7 (2C); 23.2 (2C); 27.8 (2C); 29.8 (2C); 30.0 (2C); 30.2 (5H); 31.0 (2C); 32.5 (2C); 117.7 (2C); 121.0 (2C); 121.7 (2C); 133.1 (2C); 133.4 (2C); 141.0 (2C); 155.9 (2C). IR (Nujol, cm^{-1}): 723(w), 766(w), 1238(w), 1263(w), 1300(w), 1314(w), 1377(m), 1462(m), 1520(w), 1557(m), 1595-(w), 1634(m), 1957(s), 2924(s), 2911(s), 2855(s), 3324(m). MS (D − EI+) *m/z*: 634 (M^+). Anal. Calcd for $C_{38}H_{62}N_6O_2$: C, 71.88; H, 9.84; N, 13.24. Found: C, 71.7; H, 9.8; N, 13.2.

Characterization of the Gels. In a typical gelation experiment a weighted amount of the bis-urea compound and 1 mL of the solvent are placed in a test tube, which is sealed and then heated until the compound is dissolved. The solution is allowed to cool to room temperature. Gelation was considered to have occurred when a homogeneous substance was obtained, which exhibited no gravitational flow.

For the determination of the melting points, a steel ball with a weight of 150 mg and a radius of 0.17 cm (maximum stress σ = 20 Pa) was placed on top of the gel and the vial was sealed. A series of these samples were placed in a stirred oil bath which was slowly heated (typically 2−4 °C/min) while observing the positions of the steel balls and simultaneously monitoring the temperature with the aid of a thermocouple in one of the vials. The melting point of a particular sample was taken as the temperature at which the steel ball reaches the bottom of the vial and was within ±1 °C reproducible.

For electron microscopy a small amount of a gel was deposited on a holey carbon grid, and the excess was blotted off with filter paper. The samples were vitrified by rapid plunging into a liquid nitrogen slush. The samples were transferred to a Gatan 626 cryo holder and examined at ca −170 °C in a CM10 microscope (Philips) operating at 100 kV.

For the SAXS measurements, 10 mM gels were transferred to 1 mm glass capillaries, which were flame-sealed and aged for

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24 h. The SAXS measurements were performed at 25 °C, using a NanoStar device (Bruker AXS and Anton Paar) and Cu Kα radiation.[23]

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